Microindentation characterization of polymers and polymer based nanocomposites

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POLITÉCNICA

- Hardness and hardness measurement
  - Vickers hardness
  - Relationships between hardness and other mechanical properties of polymers
  - DSI
  - Microindentation and viscoleasticity
- Microhardness of heterogeneous polymer systems
  - Microhardness of semycrystalline polymers
  - Microhardness of blends
  - Microhardness and physical ageing
  - Microhardness of PMC's
  - Microhardness of PMnC's

Hardness

- DEFINITION: a measure of the resistance to permanent surface deformation or damage.
  - Local character of measurement
  - What is the meaning of surface damage?

- METHODS OF TESTING:
  - Scratching
  - Static indentation
  - Dynamic indentation
  - ...

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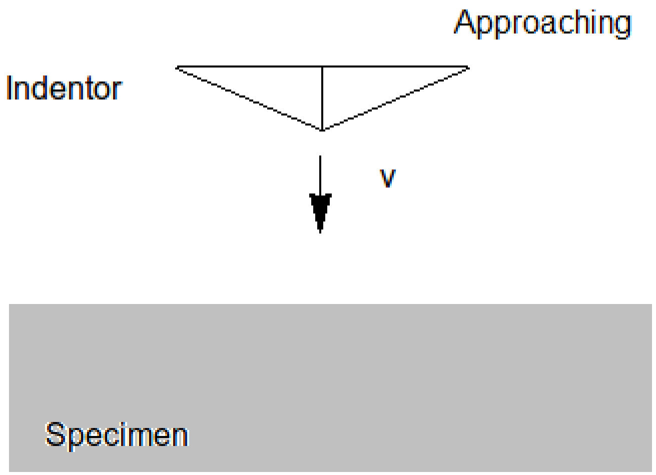
The Vickers test

- Static penetration test
- Diamond square based pyramidal indentor (angle between the faces: 136º)
  - Diamond: indentor remains undeformed during the test
  - Pyramidal: geometric similarity of indentations $\Rightarrow$ hardness is load independent
  - 136º: HV ≈ HB if HB < 600

Stages of the test



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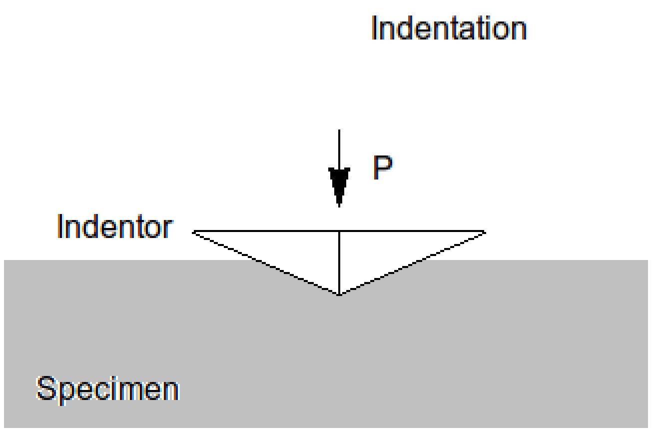

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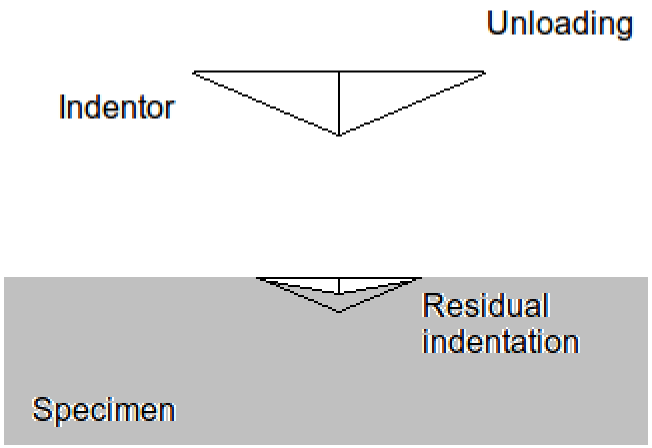


Vickers hardness definition

- Average pressure on the lateral surface of the residual indentation
- HYP.: the geometries of indentor and indentation are similar $\Rightarrow$
  - $h = d/7$ and $S_{lat} = d^2/(2.\sin 68º)$

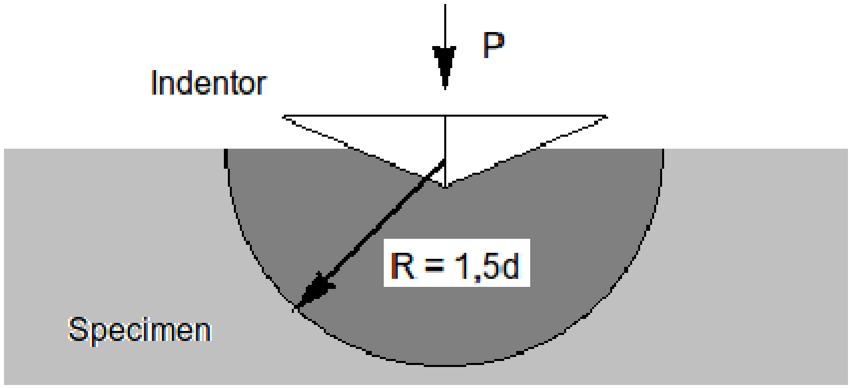
    d: diagonal of the base of the residual imprint

    h: indentation depth; S_{lat}: contact area
  - $HV = 2.\text{sen } 68º \ P/d^2$

    HV: Vickers hardness; P: load

- MICROHARDNESS: hardness measured after applying small loads (grams) $\Rightarrow$ diagonal of the residual indentation: μm

Stress distribution under the indentor



- Classical results and FEM calculations:
  - Stresses are confined to a hemispherical region with radius ≈1,5d≈10h
- Some practical considerations:
  - Minimal distance between two indentations
  - Minimal distance between indentations and edges
  - Minimal thickness of films
  - Very small sample quantity (ng)

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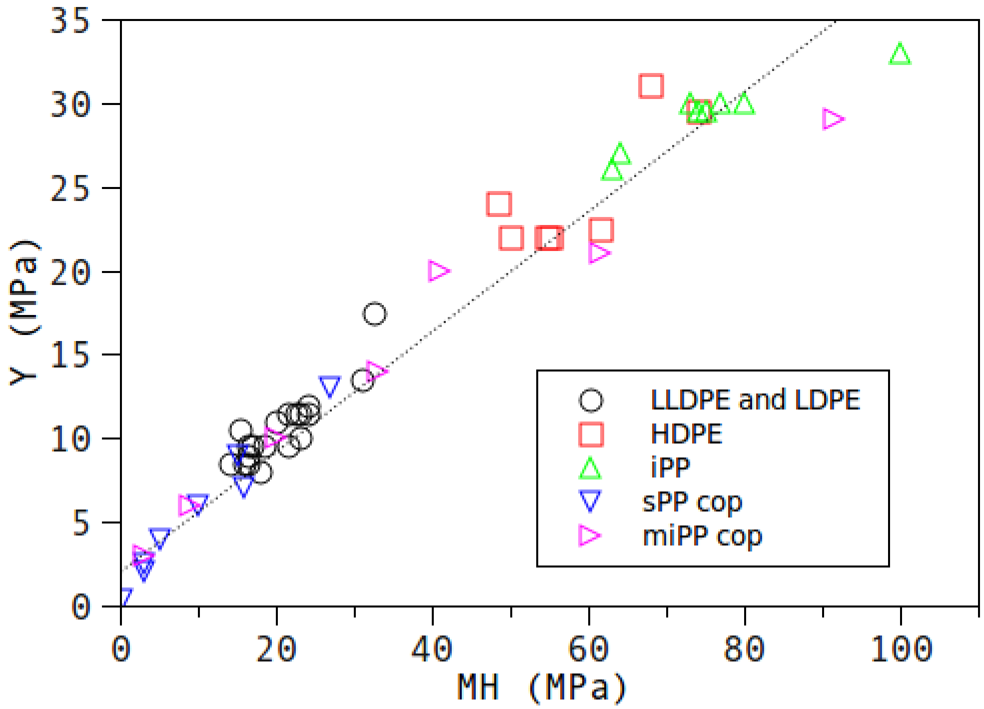
Relationships between MH and other mechanical properties



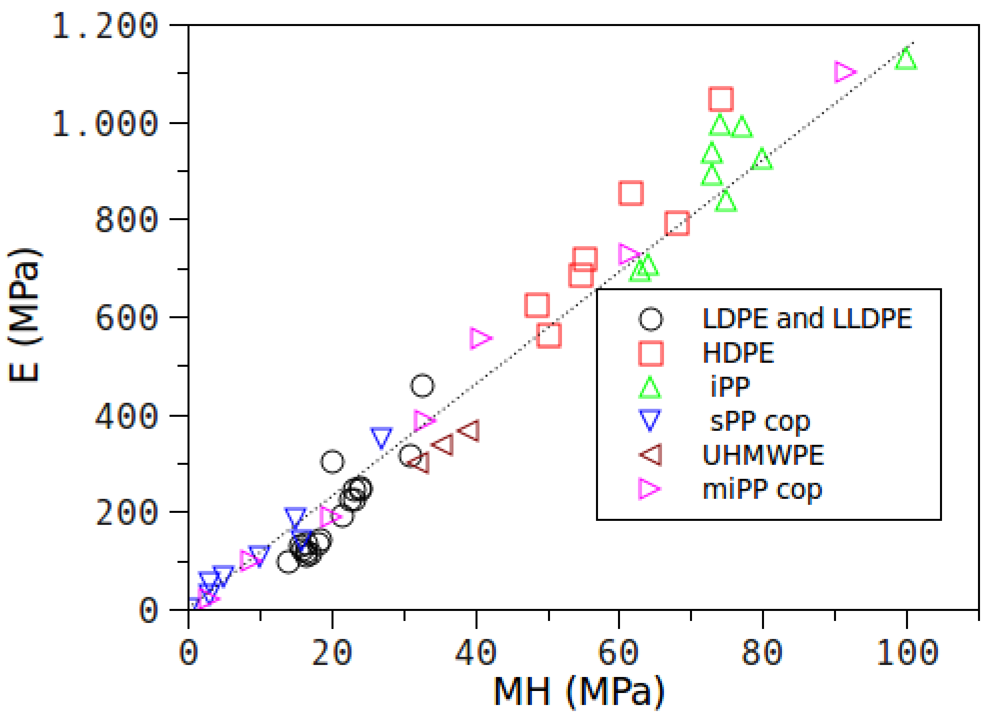
V. Lorenzo et al.: Die Ang. Makromol. Chem., 172 (1989) 25-35

V. Lorenzo et al.: J. Mater. Sci. Let., 8 (1989) 1455-1457

J. Arranz et al.: Polymer, 46 (2005) 12287-12297

Palza, H. et al.: Macromol. Chem. Phys., 209 (2008) 2259-2267

Relationships between MH and other mechanical properties



V. Lorenzo et al.: Die Ang. Makromol. Chem., 172 (1989) 25-35

V. Lorenzo et al: J. Mater. Sci. Let., 8 (1989) 1455-1457

G. Zamfirova et al.: J. Appl. Polym. Sci., 88 (2003) 1794-1798

J. Arranz et al.: Polymer, 46 (2005) 12287-12297

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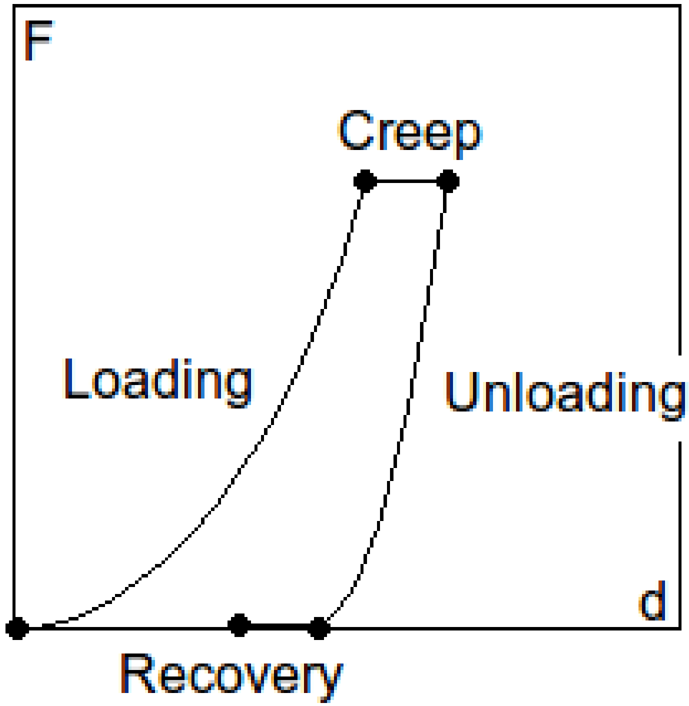
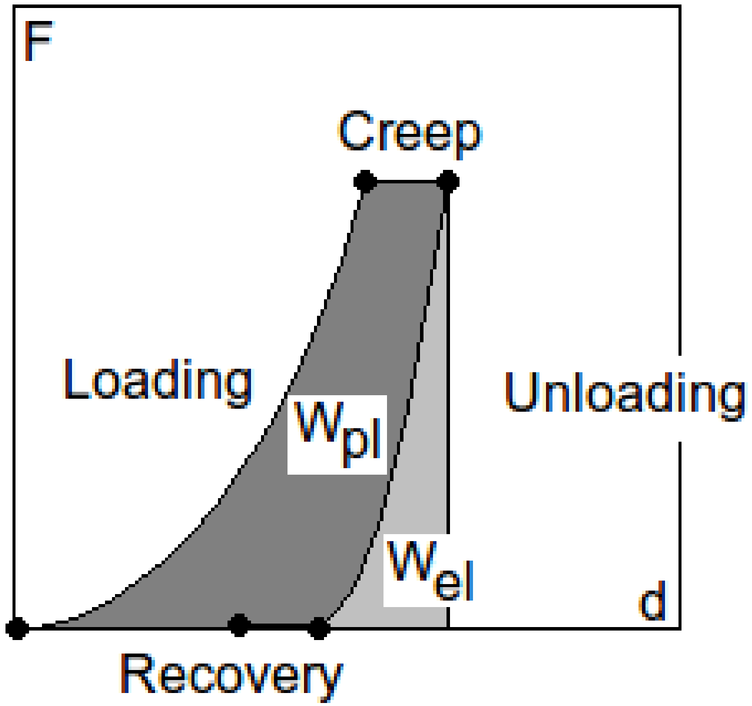
DSI: Depth Sensing Indentation



- 1980's: continuous measurements of load and indentation depth
- Very small loads (mN) $\Rightarrow$ resolution: μN
- Very small indentation depths (tenths of μm) $\Rightarrow$ resolution: nm
- Berkovich indenter

Fischer Cripps, A.: 'Nanoindentation', Springer (2004)

Results of DSI tests



- Hardness under load
- Creep
- Elastic modulus
- Delayed elastic recovery
- Deformation energy
- Recoverable energy
- …
- And, of course, hardness

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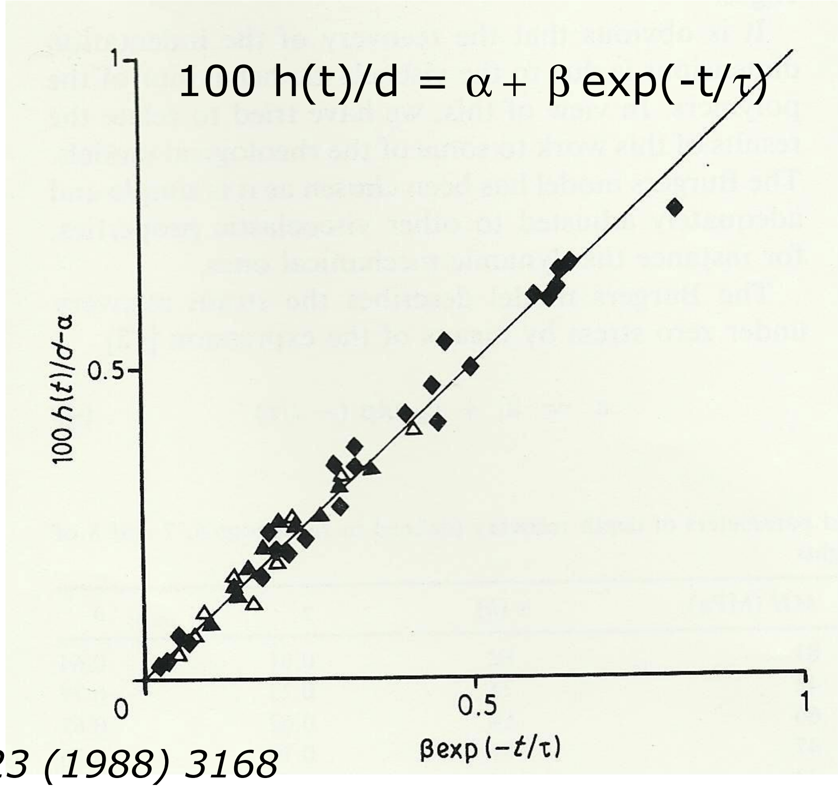
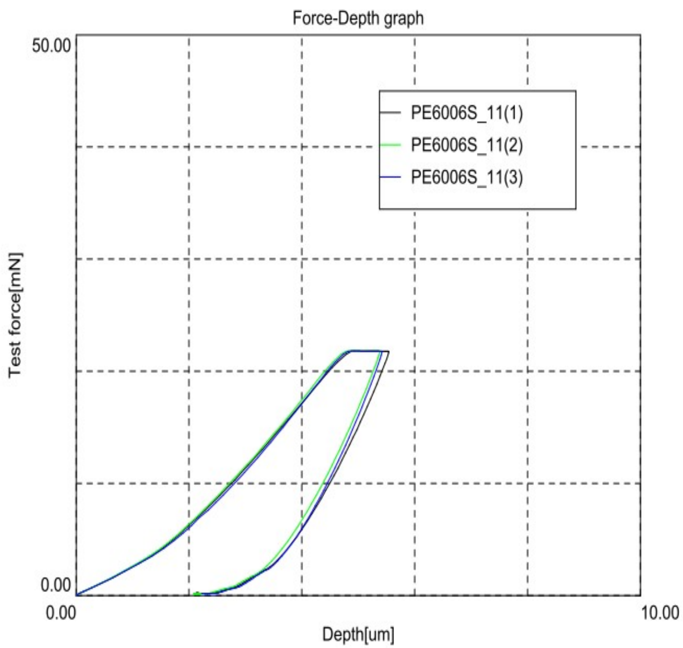
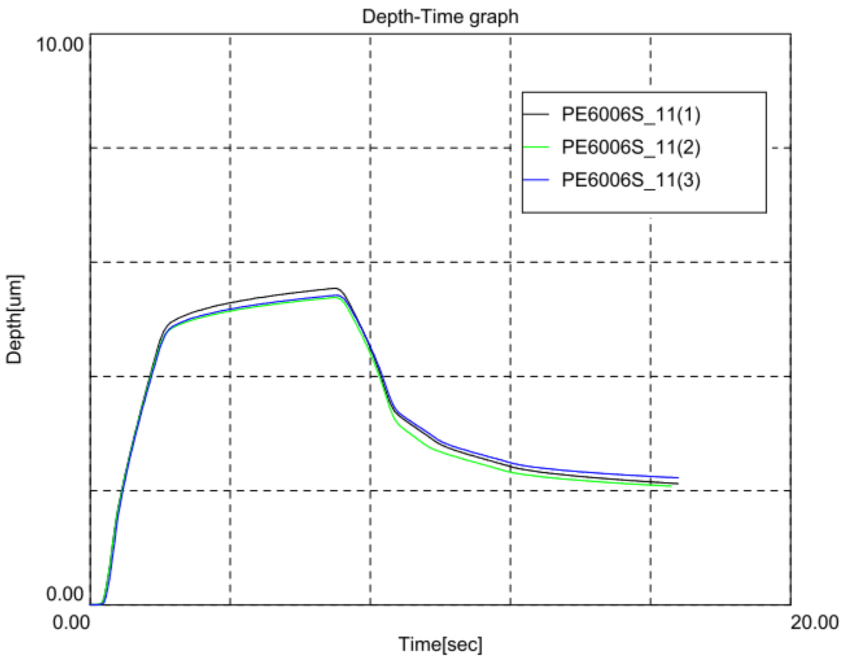
Geometry of the residual indentations on polymers



V.Lorenzo et al.: J. Mater. Sci., 23 (1988) 3168

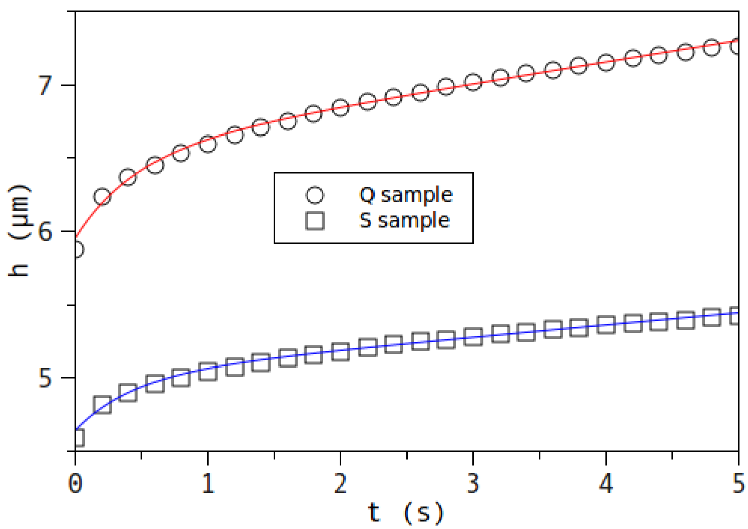
Delayed elastic recovery study by means of DSI measurements



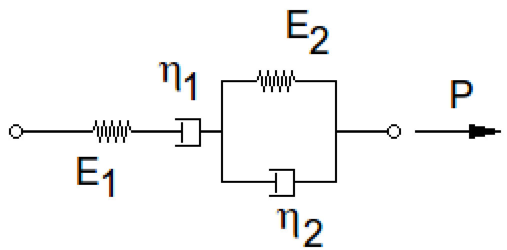


V.Lorenzo et al.: communication to EPF2011, Granada, 26th June-1st July

Creep study by means of DSI measurements



- Model:



$$h^2(t)=\frac{\pi}{2}P_0\,\mathrm{cotg}\,\alpha\left[\frac{1}{E_1}+\frac{1}{E_2}\left(1-\exp\left(\frac{E_2t}{\eta_2}\right)\right)+\frac{t}{\eta_1}\right]$$

Sample	E (MPa)	τ (s)	Cit (%)
Q	410	0,48	23
S	675	0,46	18

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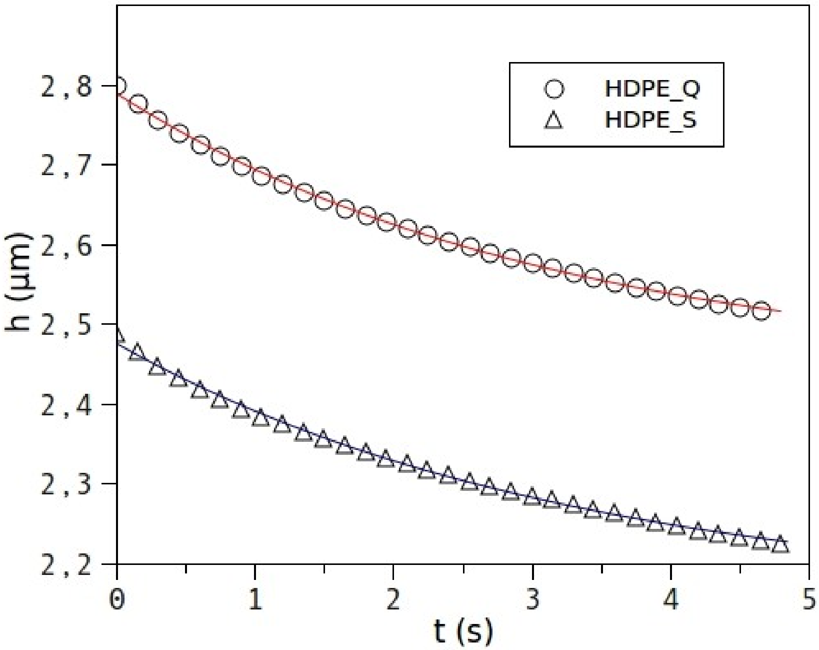

Model:

$$h(t) = h(0) + A(1 - \exp(-t/\tau))$$

- Retardation time, τ, structure independent
- Not a quantitative agreement
  - Interferometry experiments
    - Indenter geometry
    - Sampling frequency
  - Creep results:
    - Non linearity

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Local character of the measurement

- Microindentation "averages" the properties of some μm^3 of the material around the indentor.
- Microindentation and heterogeneity of the specimen:
  - Characteristic length of heterogeneities > d $\Rightarrow$ MH = f(x, y)
    - Information about distribution of phases
    - Characterization of phases
  - Characteristic length of heterogeneities < d $\Rightarrow$ MH is not a function of the position
    - Bulk properties of the material

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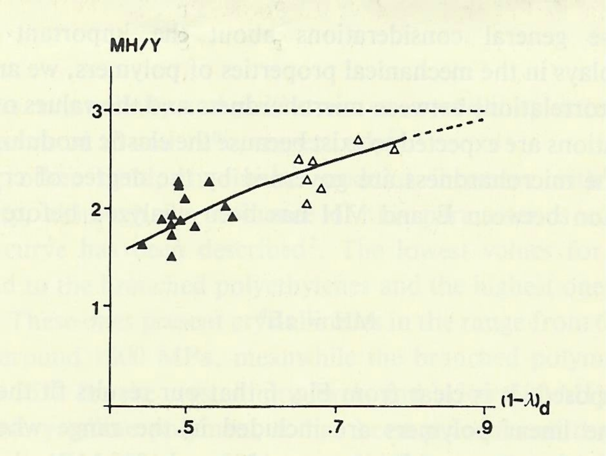
- Polyethylenes that has been quickly cooled form the melt:
  - Length of crystallites < d ⇒ MH is not a function of the position ⇒ MH is an increasing function of crystallinity level
  - Information about deformation mechanism



V. Lorenzo et al.: Die Ang. Makromol. Chem., 172 (1989) 25-35

Properties of the phases of semycrystalline polymers

- It is not possible to obtain a 100% crystalline or amorphous PE sample.
- Mechanical properties of phases can be obtained by extrapolating MH measurements

  Baltá-Calleja, F.J.; Fakirov, S., 'Microhardness of Crystalline Polymers' ; Cambridge University Press: Cambridge, 2000

- Isothermally crystallized iPP displays spherulites of the α and β polymorphs ⇒ properties of the α and β spherulites

  Seidler, S.: JOURNAL OF MACROMOLECULAR SCIENCE, Part B—Physics, B41 (2002) 851–861

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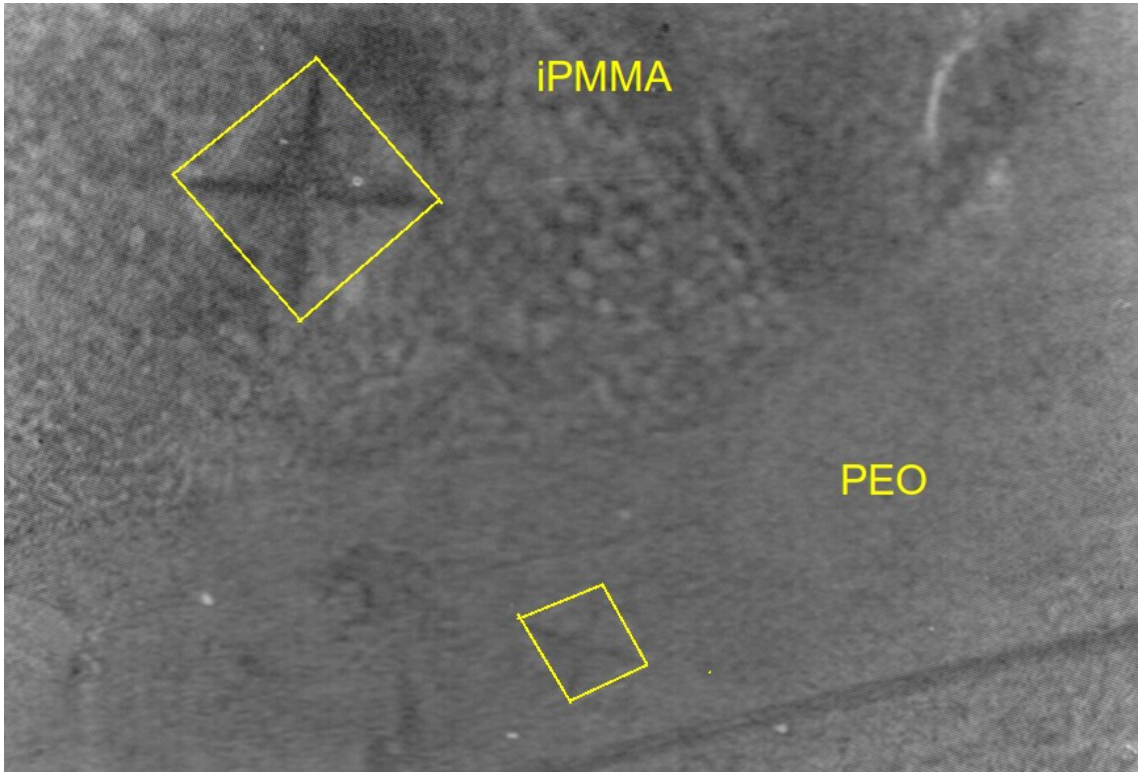
Microhardness of blends

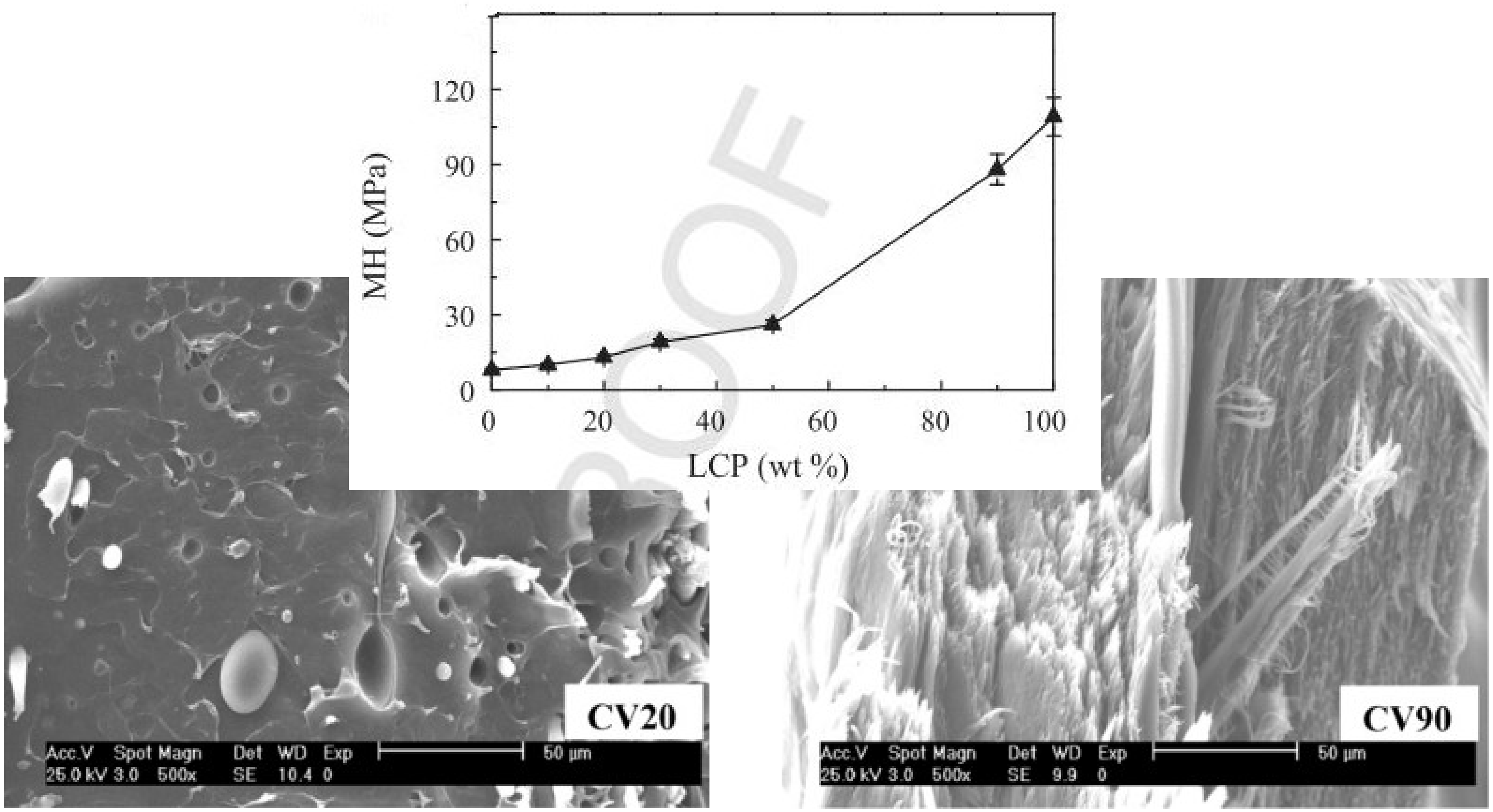
- Blends of miscible A and B polymers:homogeneous at d scale $\Rightarrow$ MH = f(%A)
- Blends of inmiscible A and B polymers: separated domains of A and B
  - If %A << %B $\Rightarrow$ characteristic length of A domains < d $\Rightarrow$ MH is a continuous function of %A
    - Continuity of MH(%A) $\not\Rightarrow$ miscibility
  - If %A is comparable con %B:
    - Characteristic length of A domains < d
    - Characteristic length of A domains > d
      - MH is a function of the position
      - Characterization of individual phases

Microhardness of blends of PEO with iPMMA



V. Lorenzo et al.: J. Mater. Sci. Lett., 9 (1990) 1011-1013

Microhardness of blends of polyolefins and LCP's



J. Arranz et al.: doi:10.1016/j.memsci.2011.04.023

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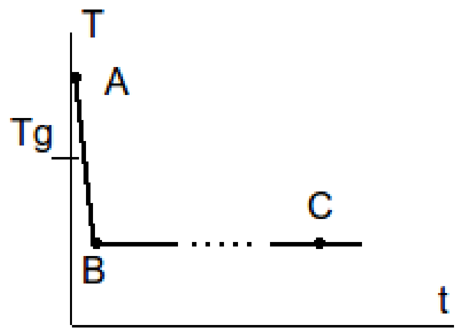
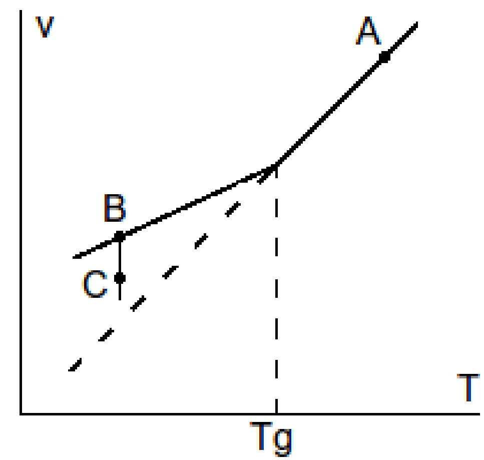
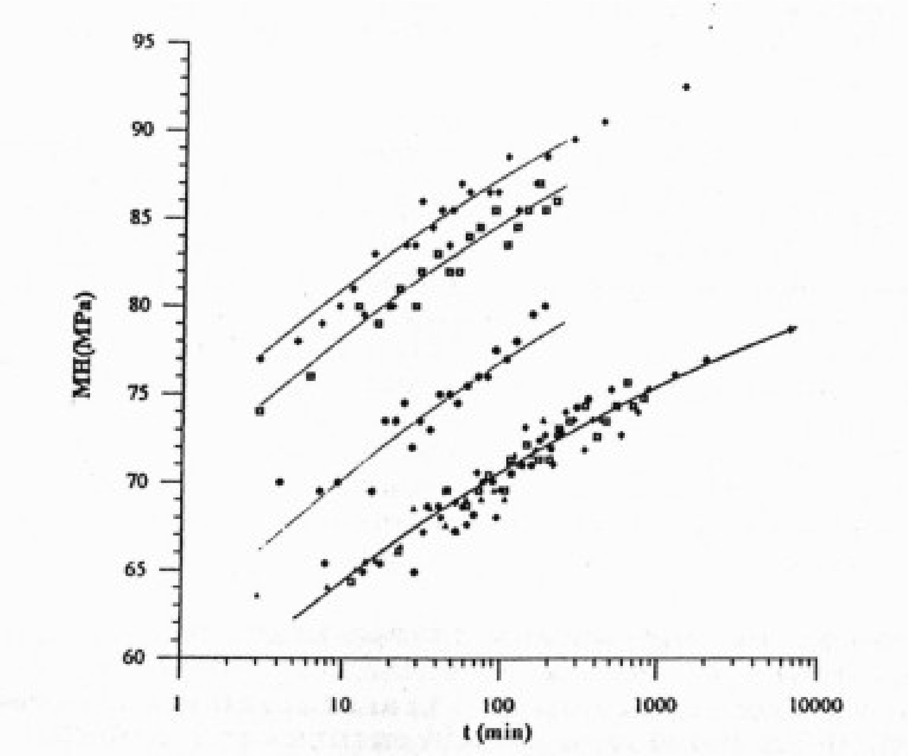
Microhardness and physical ageing

- A – Tg: liquid
  - Cooperative movement of chains
- Tg – B: glass
  - Movements of local groups
- B – C: physical ageing
  - Densification:
    - Local free volume fluctuations
    - Correlation length < 10^{-1} μm

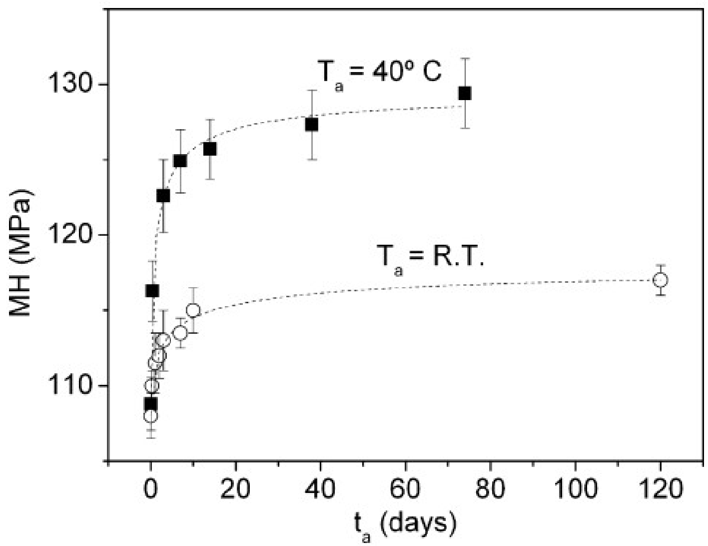




Physical ageing of LCP's and SMP's as revealed by MH tests



A. Ormazábal et al. In "Nanostructured and Non-Crystalline Materials", World Scientific, Singapore (1995) 202-206



V. Lorenzo et al.: Materials and Design 30 (2009) 2431–2434

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Microhardness of polymeric matrix composites

- Composites are multiphasic materials: fillers dimesions ~ some tens of μm $\Rightarrow$ characteristic dimensions of heterogeneities > d $\Rightarrow$ MH is position function $\Rightarrow$ MH is not an adequate tool for characterizing composite materials

But it can be used for:

- Characterizing matrix and fillers.
- Characterizing interphases:
  - Transcrystalline structures in GF reinforced PP composites

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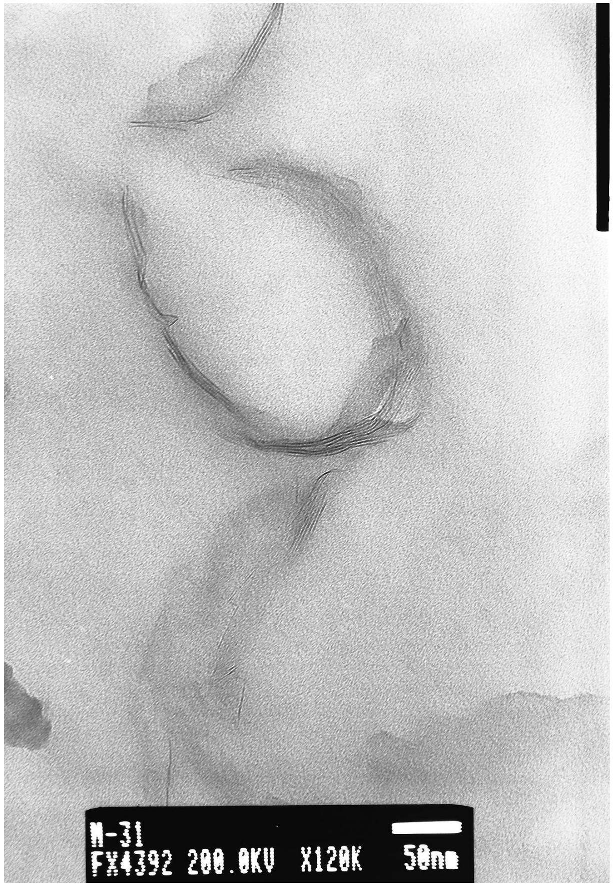
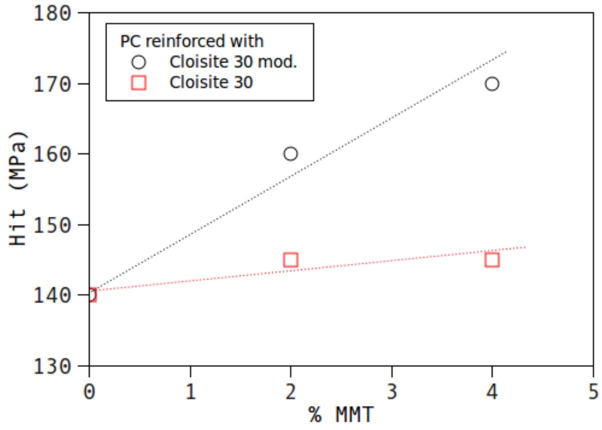
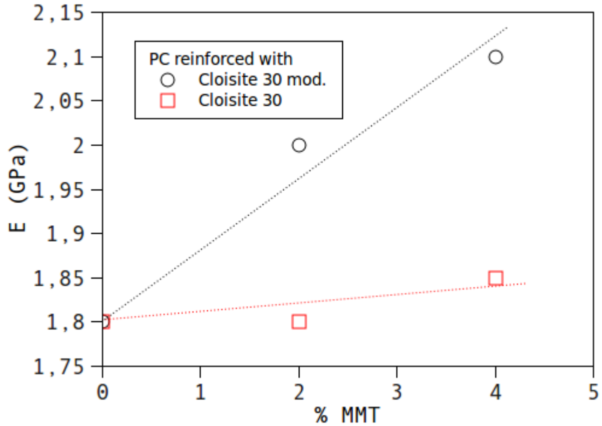
Microhardness of nanocomposites

- Aglommerated fillers:
  - characteristic length of heterogeneities $> d \Rightarrow$ MH is a function of position
- If the fillers are well dispersed:
  - characteristic length of heterogeneities $< d \Rightarrow$ MH = f(% filler) $\Rightarrow$ information about the reinforcement effect of the filler.

PC-clay nanocomposites obtained by disolution

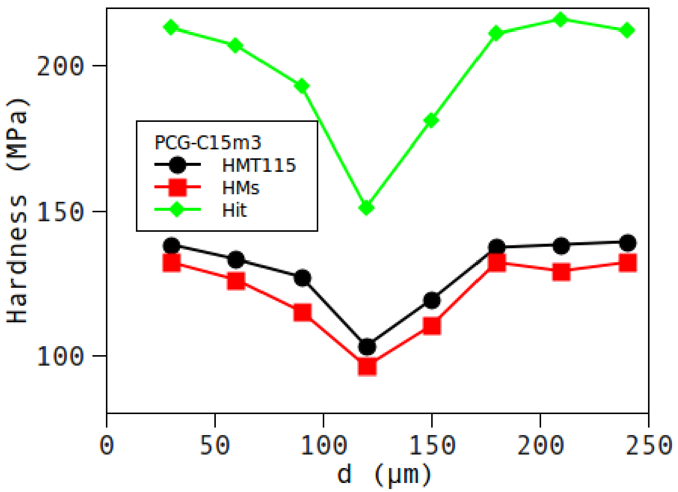






Other heterogeneous polymeric materials

- Characterization of coatings
- Multi-layer extrusion
- Skin-core structures in injection molded polymers
- Composition gradients
- ...



Summarizing

- Microindentation is an adequate tool for exploring structure of polymeric materials
- The volume of material that is deformed in hardness test is around d^3
- The information that can be obtained from a hardness test depends on the characteristic length of the heterogeneities of the sample, l:
  - If l < d, bulk porperties of the material
  - If l > d, local character information

The research group

- ICTP (CSIC)
  - Prof. J.M. Pereña
  - Prof. R. Benavente
  - Prof. E. Pérez
  - Prof. M.L. Cerrada
  - Dr. J. Arranz
- ETSII (UPM)
  - Prof. J. Martínez
  - Prof. De la Orden
  - Prof. G. Pinto
  - Prof. V. Lorenzo

and all the postdoc, students and technicians that have collaborated with us.

Thank you very much for your attention

Merci pour votre attention

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